First Principles Analysis of the Elementary Reaction Paths for Fischer Tropsch Synthesis over Co and Ru

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There has been a strong resurgence of interest in Fischer Tropsch (FT) synthesis over the past decade since Fischer Tropsch provides a viable route to ultraclean fuels. This eliminates the production of NO_x and SO_x by-products. FT synthesis offers the ability to create a wide range of different reaction products including olefins, gasoline, diesel fuel, waxes and oxygenates. Despite the tremendous number of developments in FT synthesis, there are still many unanswered questions concerning the mechanism which makes it difficult to engineer catalytic materials that are highly active result in the selective product distributions. Theory and simulation have advanced to the stage where they can begin to greatly complement experimental efforts by probing the elementary steps. In this work, we hope to develop an ab initio-based kinetic simulation algorithm that will allow us to probe a number of unanswered issues concerning FT synthesis over supported bimetallic CoRu particles.

The objectives are to: 1) understand the reaction mechanisms that control FT kinetics, 2) predict how the intrinsic metal-adsorbate bond affects the sequence of elementary steps in FT, 3) establish the effects of the reaction environment on catalytic activity and selectivity, 4) construct a first-principles based tool that can incorporate the detailed atomic surface structure and simulate the kinetics for the myriad of elementary pathways that make up FT chemistry, and 5) suggest a set of optimal features such as alloy composition and spatial configuration, oxide support, distribution of defect sites.

Accomplishments from First 9 Months

In the first phase of this work, we have used periodic gradient corrected density functional quantum chemical methods to calculate the chemisorption energies, activation barriers and overall reactions energies for a set of steps that make up the initial phases of the reaction mechanism.

We have calculated the chemisorption energies for a comprehensive set of hydrocarbon intermediates involved in FT chemistry including, CO*, H*, CH_x*, C_2H_x*, O*, H_2O*, OH* over different Co and Ru surfaces. The results indicate that these intermediates tend to bind more strongly to Ru than Co as might be expected. There are, however, some outliers to this trend.

CO dissociation occurs more readily over Ru than over Co. The barriers over Co (~230 kJ/mol) and Ru(~150 kJ/mol) are sufficiently high that the direct dissociation over the ideal terraces is highly unlikely. Step edges and defect sites can lower surface coverages help to dramatically lower the barriers of activation and are likely important sites for CO activation. CO dissociation over RuCo alloys lie between those of CoRu and therefore appear to offer any enhancement, at least for the two alloys examined.

The hydrogenation of CH* and CH_3* appear to be the most difficult steps in successively moving from C* to CH_4. The CH* group is the most stable species on the surface. Activation of CH* to C* is quite difficult. In general the activation barriers for hydrogenation over Co appear to be lower than those for hydrogenation over Ru by about 3-4 kcal/mol.

Hydrocarbon coupling reactions were also found to be significantly lower over Co(0001) than over Ru(0001). Coupling again involves breaking the metal adsorbate bond. Metal-CHx bonds are significantly stronger on Ru than they are on Co as might be expected since Ru has a somewhat more vacant d-band. This would indicate that the coupling of CH_x* fragments would be more difficult over Ru. This is consistent with our results shown herein our computational results. These results are consistent with the hydrogenation results in that the coupling of CHx* with H* is also more difficult over Ru. Hydrogenation, however, is a little less sensitive. This is due to the fact that M-H bond strength for Co and Ru are similar.

A direct comparison between Co and Ru at this stage, however, would not indicate anything about the relative product distributions at this stage. The product distribution is critically dependent on the balance between all of the reaction steps, and thus will require simulating all of the elementary surface processes.

2. A List of Published Journal Articles, Completed Presentations and Students Receiving Support from the Grant

This grant was used to support Dr. Qingfeng Ge to carry out the work.